

## LECTURE

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## Electron spectroscopic investigation of Sn coatings on glasses

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**Abstract** Float glasses of different thicknesses and a conducting tin oxide glass have been investigated using Photo and Auger Electron Spectroscopy induced by  $\text{AlK}\alpha$  X-rays. On the basis of measured chemical XPS shifts in the binding energies the chemical state of Sn (+2 or +4) incorporated on the float glasses could not be assigned. The use of the Auger parameter allows to separate relaxation and chemical contributions. The derived true chemical shifts of Sn on float-glasses are larger than those of  $\text{SnO}$  and/or  $\text{SnO}_2$  due to the larger ionic environment of the glass matrix.  $\text{Ar}^+$  or HF etching reveals that the concentration of Sn decreases exponentially as a function of depth from the surface.

### Introduction

Coating of Sn and its oxides plays a very important role in technologically important applications like float-glass production, solar energy cells, protective and conductive coatings, etc.. Numerous electron spectroscopic investigations dealing with tin oxides have been reported [1–4]. For many applications quantitative data for Sn, like surface coverage or depth profiling, are important parameters. In some applications, however, further information like oxidation state, coordination number, etc., are needed. XPS and/or AES studies

attempting to distinguish between the two oxides of tin,  $\text{SnO}$  and  $\text{SnO}_2$ , showed either the absence or only a small difference in the core level binding energies [1–4]. In a different investigation, it was demonstrated that, although the core level shifts were not significant, XPS of the valence band region helped unambiguously to distinguish between the two oxides [5]. Another parameter which can be derived from the X-ray induced photoelectron spectra is the Auger parameter. The concept of the Auger parameter, introduced by Wagner [6] and further developed by others [7, 8], can be very informative. In a recent study [9], we have reported the Auger parameters of tin metal, tin oxides and chlorides. In this study we extend our study to float glasses of different thickness and a tin oxide coated conducting glass. Tin is incorporated on both surfaces of glasses produced by the float technique (float glasses). Incorporation of tin on the tin-bath surface of the glass is achieved by contact with liquid tin and is homogeneous, while the atmospheric surface is known to be produced by precipitation of tin vapors and in form of islands [10].

### Experimental

Float glasses with thicknesses of 3, 4, 5, 6 and 10 mm were provided by the local producer (Türkiye Şişe-Cam A.Ş.), while the conducting tin oxide glass is a commercial tin oxide glass. Electron spectroscopic measurements were carried out with a KRATOS ES300 spectrometer using  $\text{AlK}\alpha$  X-rays. Samples of the appropriate size were wiped by a clean tissue paper before their introduction into the spectrometer. Pressure in the analyzer chamber was kept below  $5 \times 10^{-9}$  Torr during analysis. Depth profiling was carried out using either (i) in-situ  $\text{Ar}^+$  etching with 1 keV ions or (ii) etching with a 2% HF solution before introduction into the spectrometer.

Both the  $\text{C1s}$  peak (B.E. = 285.0 eV) from residual hydrocarbons and the  $\text{Si2p}$  peak (B.E. = 103.2 eV) were used as reference for charging effects. The accuracy in binding energies is around 0.1 eV while for the Auger parameter it is believed to be 0.05 eV due to suppression of charging effects. Quantitative data were obtained using standard procedures [11].

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## Results and discussion

Figure 1 displays a typical electron spectrum of a float glass induced by  $AlK\alpha$  X-rays. Photoelectron lines corresponding to O1s, C1s, Si 2s and 2p, Ca 2s and 2p, Sn 4d, 3d and 3p lines as well as O, Na and Mg KLL and Sn MNN (not shown in the figure) Auger lines are the prominent features. Na KLL Auger and Sn 3d<sub>3/2</sub> lines overlap but can easily be separated by curve resolution.

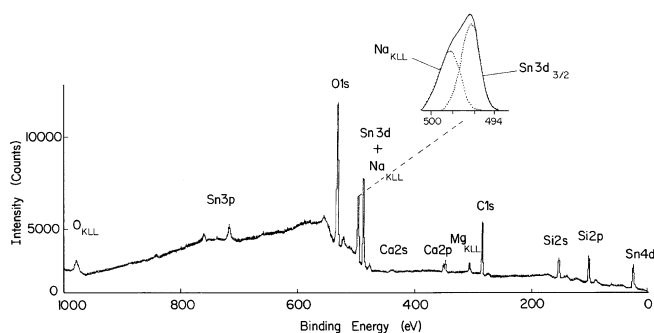
The intensities of the Sn lines vary depending on the surface examined (i.e. tin-bath or atmospheric), the thickness of the glass and naturally the etching time. The relevant data are collected in Table 1. The table also contains data on SnO, SnO<sub>2</sub> as well as the tin oxide conducting glass.

### Chemical state of Sn

The measured binding energies of SnO, SnO<sub>2</sub> and Sn on glasses are very close to each other. On the basis of the raw binding energies of Sn one can not, unambiguously, decide on the chemical state of Sn. The measured binding energies contain contributions from relaxation effects besides the chemical shifts. At this point we must refer to the Auger parameter or the true chemical shift. Figure 2 gives the Sn MNN Auger spectra of SnO<sub>2</sub> (a), SnO (b) and the conducting glass (c). It is evident from the figure that the Auger lines display a much larger (close to 1 eV) chemical shift. We can analyze the chemical shifts in binding energies,  $\Delta E_{ch}$ , using Wagner's approach of identifying compounds on the basis of their Auger parameters:

$$\alpha = E_b + E_k$$

where  $E_b$  is the binding energy of the photoelectron and  $E_k$  is the kinetic energy of the Auger electron emitted as a result of the Auger process involving the same electron level. The shift in  $E_b$  can be regarded as the sum of (i) the chemical shift,  $\Delta E_{ch}$ , which depends on the effective



**Fig. 1**  $AlK\alpha$  X-ray induced electron spectrum of the tin-bath side of a 3 mm float glass, *Insert* shows the overlapping Na KLL Auger and Sn 3d<sub>3/2</sub> photopeaks

tive charge of the atom, and (ii) the relaxation energy. The latter consists of two components, intra and extra atomic relaxations,  $E_{ir}$  and  $E_{er}$ , determined by the interaction of other electrons within the same atom or its neighbours. One can roughly describe them as gas phase (intra-atomic) and solid-state (extra-atomic) contributions. If  $E_{ir}$  is constant, one obtains the binding energy shift in relation to zero-valent bulk material (Sn metal in the case of tin):

$$\Delta E_b = \Delta E_{ch} + \Delta E_{er}$$

Contributions to the chemical and relaxation terms of the Auger electrons can be expressed as follows:

$$\Delta E_k = -\Delta E_{ch} + 3\Delta E_{er}$$

$$\Delta\alpha = -\Delta E_b + \Delta E_k$$

$$\Delta\alpha = 2\Delta E_{er}$$

This procedure allows to separate chemical (the true chemical shift) and relaxation contributions from the measured binding energies and Auger parameters.

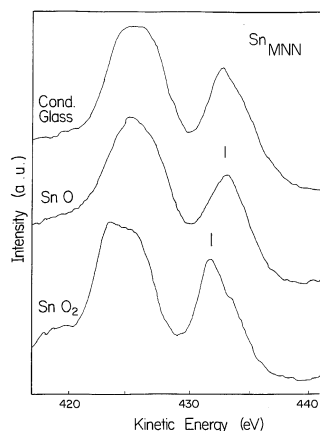
As can be seen from the table, the chemical shift computed using this procedure is 0.2 eV for SnO and 0.3 eV for SnO<sub>2</sub>. For Sn coated on glasses, however, the derived shifts vary between 0.5 and 0.8 (except for the

**Table 1** XPS/XAES data of some float glasses, the tin oxide conducting glass together with some reference compounds (Referenced to Si2p = 103.2 eV)

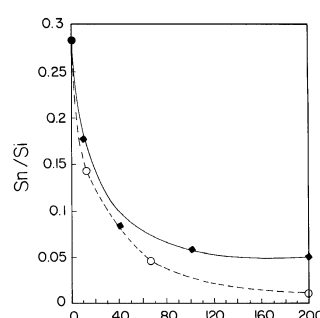
	BE (eV) Sn3d <sub>5/2</sub>	KE (eV) SnMNN	$\alpha_{Sn}$ (eV)	$\Delta E_{er}$ (eV)	$\Delta E_{ch}$ (eV)	Atomic ratio	
						Sn/Si	O/Si
3 mm	488.2	430.5	918.7	−1.7	0.8	0.283	4.12
3 mm (at.surf.)	487.7	430.6	918.3	−2.0	0.1	0.026	3.12
4 mm	488.1	430.7	918.8	−1.8	0.7	0.235	3.12
5 mm	488.0	430.5	918.5	−1.9	0.5	0.193	4.68
6 mm	488.1	430.2	918.3	−2.0	0.5	0.164	3.93
10 mm	488.1	430.5	918.6	−1.8	0.7	0.222	3.22
Cond. Glass <sup>a</sup>	487.6	431.9	919.5	−1.4	0.6	—	2.58
Sn <sup>a</sup>	485.6	436.7	922.3	—	—	—	—
SnO <sup>a</sup>	487.1	433.0	920.0	−1.3	0.2	—	0.98
SnO <sub>2</sub> <sup>a</sup>	487.5	431.6	919.1	−1.6	0.3	—	1.66

<sup>a</sup> Referenced to C1s = 285.0 eV

**Fig. 2** Sn MNN Auger peaks of SnO<sub>2</sub> (bottom), SnO (middle) and the tin oxide conducting glass (top) induced by AlK $\alpha$  X-rays



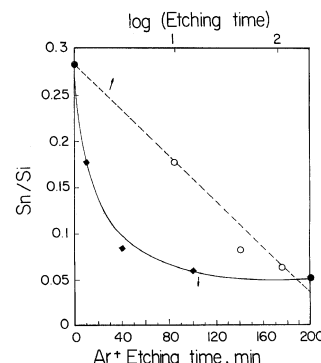
**Fig. 3** Ratio of the Sn/Si concentration of a 3 mm float glass as a function of  $\blacklozenge$  etching time [min] (Ar<sup>+</sup>),  $\circ$  etching time [s] (2% HF)



tin on the atmospheric side of the glass) and are larger than that of SnO<sub>2</sub>. This can be understood if one considers that Sn atoms in the glass matrix are in a stronger ionic environment compared to the oxides. It is also evident that Sn on the atmospheric surface of the glass, which is presumably formed via precipitation from vapor phase, has an entirely different chemical nature (only 0.1 eV chemical shift).

The Sn on the surface of the conducting tin oxide glass exhibits a 0.6 eV chemical shift and hence has a resemblance to that of Sn on float-glasses. However, the Auger spectrum, as shown in the upper part of Fig. 2, and the X-ray diffraction pattern [9] suggest that it is a mixture of SnO and SnO<sub>2</sub>.

**Fig. 4** Sn/Si ratio plotted against Ar<sup>+</sup> etching time in a linear ( $\circ$  bottom) and log ( $\blacklozenge$  top) version



### Sn depth profile

The ratio Sn/Si as determined from the Sn 3d<sub>5/2</sub> and Si 2p lines of a 3 mm float glass are plotted in Fig. 3 as a function of the etching time using both Ar<sup>+</sup> and HF solution. The good fit to the semi-logarithmic plot in Fig. 4, is a demonstration that incorporation of Sn onto the tin-bath surfaces is diffusion-controlled.

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